1893

On the Decomposition of Diazo Compounds: VII. On the Reaction of Alcohols with Paradiazobenzene Sulphonic Acid

William Bush Schober

VOL. XV. [JUNE, 1893.] No. 6.

AMERICAN

CHEMICAL JOURNAL.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

VII.—ON THE REACTION OF ALCOHOLS WITH PARADIAZOBENZENESULPHONIC ACID.[1]

BY W. B. SHOBER.

This investigation was undertaken at the suggestion of Professor Remsen, and carried on under his guidance, with the object of determining the action of methyl, ethyl and propyl alcohols on paradiazobenzenesulphonic acid, at various pressures.

16 grams of the diazo compound were boiled with about 250 cc. of methyl alcohol (distilled from lime) under a pressure of 760–780 mm. of mercury. At first the alcohol assumed a yellow color, then changed to pink, and finally the liquid became dark red. The decomposition was slow, about two and a half hours being necessary to decompose all of the diazo compound. The liquid obtained in this way is very strongly acid. The alcohol was distilled off, leaving a dark syrupy residue. Repeated attempts to obtain crystals from this residue, after purification with animal charcoal, were unsuccessful. The residue was dissolved in water and boiled with animal charcoal, nearly all the color being removed by this means. It was then neutralized with barium carbonate; a slight precipitate of barium sulphate was formed which was filtered off. The sodium salt, or rather salts (for, as shown below, two reactions took place), were made by precipitating the barium as carbonate. It was found necessary to use

[1] From the author's thesis for the degree of Doctor of Philosophy. Submitted to the Board of University Studies of the Johns Hopkins University, June, 1892.

the sodium compound, as the corresponding barium salts do not react readily with phosphorus pentachloride. The sodium salts were treated with one molecule of phosphorus pentachloride. The action takes place easily without the aid of heat. When the reaction was completed the flask containing the products was heated to 120° in a sulphuric-acid bath, in order to drive off the phosphorus oxychloride. The sulphonic chlorides were washed with a large amount of water. Concentrated ammonium hydroxide was then poured over the oil and the mixture allowed to stand for some time. The amides thus obtained were boiled with animal charcoal and recrystallized several times. Two different kinds of crystals were found which were separated by mechanical means. One substance crystallized in beautiful, long, slender needles, the melting-point of which was found to be 113°. This substance is shown by the analysis given below to be methoxybenzenesulphonamide, presumably the para modification, a compound which I believe has not been described before. The other compound found also crystallizes in needles, but they are much smaller. Its method of formation and melting-point (154°) show it to be parabenzenesulphonamide. The substance melting at 113° is insoluble in cold water, easily soluble in hot water and in alcohol. Analysis shows its composition to be $C_7H_9SNO_3$. The results obtained are as follows:

I. 0.29537 gram of the substance gave 0.36758 gram barium sulphate, corresponding to 17.10 per cent. of sulphur.[1]

II. 0.12373 gram of the substance gave 0.15517 gram of barium sulphate, corresponding to 17.23 per cent. of sulphur.[1] These determinations were made by Liebig's method.

I. 0.21172 gram of the substance gave 0.34615 gram of carbon dioxide and 0.08958 gram of water.

II. 0.18255 gram of the substance gave 0.29735 gram of carbon dioxide and 0.08292 gram of water.

For $C_7H_9SNO_3$:

		Theory.	Found. I.	Found. II.
C_7	83.79	44.89	44.58	44.41
H_9	9.00	4.82	4.71	5.15
S	31.98	17.13	17.10	17.23
N	14.01	7.51	7.26	7.58
O_3	47.88	25.65		
	186.66	100.00		

[1] Messrs. Hunter and Collier kindly made these determinations for me.

The compound is, therefore, methoxybenzenesulphonamide, and since it is obtained from sulphanilic acid in which the amido and sulphonic acid groups are in the para position, it is para-methoxybenzenesulphonamide.

Besides the methoxy compound there is also formed benzenesulphonic acid. Consequently the product obtained from the decomposition of the diazo compound is a mixture. Since the amides of these two acids are well crystallized substances, an attempt was made to separate them by fractional crystallization, in order to form a definite idea as to the relative quantities formed in the decomposition. This attempt was unsuccessful, owing to the fact that both amides are about equally soluble in water, alcohol, ether, and mixtures of alcohol and water in various proportions. The following experiments were made with the object of finding a method for separating the two acids:

A quantity of the diazo compound was decomposed with methyl alcohol at a pressure of 760–780 mm. of mercury. After the reaction was completed, the excess of alcohol was distilled off, the syrupy residue diluted with water and treated with animal charcoal. A portion of this product was neutralized with barium carbonate. The solution of the barium salts was evaporated to dryness and the residue boiled with alcohol. A portion dissolved.

Analysis of the portion soluble in alcohol:

0.1713 gram of the substance gave 0.0825 gram of barium sulphate, corresponding to 28.33 per cent. of barium. The theoretical per cent. of barium in barium methoxybenzenesulphonate is 26.83, and in barium benzenesulphonate, 30.40.

Analysis of portion insoluble in alcohol:

0.12275 gram of the substance gave 0.0574 gram of barium sulphate, corresponding to 27.50 per cent. of barium. Similar experiments were made, using methyl alcohol as the solvent, with the following results:

0.15112 gram of the substance soluble in methyl alcohol gave 0.074 gram of barium sulphate, corresponding to 28.80 per cent. of barium.

0.14215 gram of the substance insoluble in methyl alcohol gave 0.07071 gram of barium sulphate, corresponding to 29.26 per cent. of barium.

It is evident from these results that the barium salts cannot be separated in this way.

Attempts to separate the two Acids by means of the Anilides.—Aniline was added slowly to the chlorides; action took place with evolution of heat. The anilides thus obtained were washed with dilute hydrochloric acid, and afterward with a *small* quantity of caustic soda. Care must be taken not to use too much of this reagent, as it dissolves the anilides. Water is used to remove the caustic soda. The anilides were then crystallized from water, or preferably, from a mixture of equal parts of water and alcohol. Two kinds of crystals were deposited, small needles and irregular shaped plates, but I was unable to obtain a satisfactory separation in this way.

The following salts of the two acids were then prepared: barium, sodium, ammonium, potassium, calcium, silver, lead, copper, and zinc.

The barium, calcium, lead, and zinc salts were prepared by neutralizing the acids with the corresponding carbonates. The sodium, ammonium, and potassium salts were made from the barium salts by precipitating the barium as carbonate; the copper[1] and silver salts by precipitating the barium salts with the corresponding sulphates. It was found impossible to separate satisfactorily any of these salts by fractional crystallization.

An attempt was then made to obtain an idea of the relative amounts of the two acids formed in the decomposition of the diazo compound with methyl alcohol, by converting the products into the barium salts, determining the percentage of barium in the mixture of the two, and upon the basis of the results thus obtained to draw a conclusion as regards the relative quantities of the different acids obtained in the decomposition. With this object in view I made the following barium determinations:

I. 0.07865 gram of the barium salts gave 0.03675 gram of barium sulphate, corresponding to 27.48 per cent. of barium.

II. 0.1174 gram of the barium salts gave 0.05485 gram of barium sulphate, corresponding to 27.47 per cent. of barium.

III. 0.13885 gram of the barium salts gave 0.0645 gram of barium sulphate, corresponding to 27.32 per cent. of barium.

Six determinations of this kind were made, but, owing to variations in the results, not due to errors of analysis, no satisfactory conclusions could be drawn. Owing to a lack of time I was unable to continue experimenting along this line, and in consequence a

[1] Freund: Ann. Chem. (Liebig) **120**, 80.

method for the separation of the products of the decomposition of the diazo compound with methyl alcohol has not been found. However, the following experiments will show conclusively the conditions favorable for the formation of the methoxy compound.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 850 *mm. of Mercury.*

26 grams of the diazo compound and 520 cc. of methyl alcohol, distilled from lime, were placed in the pressure-flask. Heat was applied until a pressure of 850 mm. (the highest pressure that could be obtained with the apparatus used) was indicated by the manometer. The decomposition was complete in two and a half hours. The alcohol was then distilled off and the dark red liquid residue treated with animal charcoal. It was then converted into the amides as above described. Only a partial separation of the amides could be effected, but it was sufficiently complete to show the presence of the paramethoxybenzenesulphonamide in larger quantities than the benzenesulphonamide.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 360 *mm.*

26 grams of the diazo compound and 520 cc. methyl alcohol were placed in the flask and heated until the pressure indicated was 340–360 mm. The experiment was carried out as above. The decomposition was much slower, the time required being a little more than five hours. The products of decomposition were transformed into the amides. The quantities of the methoxy- and hydrogen-amides were about equal.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at Ordinary Pressure.

10 grams of the diazo compound and 200 cc. methyl alcohol were placed in a flask to which was attached an inverted condenser. The flask was heated on a water-bath. The action took place slowly and was complete in three hours. The products of decomposition were treated as above. Two amides were obtained, the hydrogen-amide being present in larger quantity than the methoxy-amide.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at Diminished Pressure.

The apparatus used in this experiment was devised by Mr. R. M. Parks, of this laboratory, and used by him in his study of the action of methyl alcohol on paradiazoorthotoluenesulphonic acid.[1] It is very simple and answers the purpose for which it is intended, admirably.

10 grams of the diazo compound and 200 cc. methyl alcohol were placed in the flask, which was heated on a water-bath. The experiment was conducted in the ordinary way, the pressure being 450 mm. less than the atmospheric pressure. Eight hours were required to effect complete decomposition. The product was converted into the amide. But *one* amide was formed, the melting-point of which (154°) was that of benzenesulphonamide, showing that the hydrogen reaction only took place.

These experiments led to the conclusion that if a sufficiently high pressure could be obtained, the decomposition would result in the formation of the methoxy compound only. With this object in view I made the next experiment.

Action of Methyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 30 Atmospheres.

1 gram of the diazo compound and 10 cc. methyl alcohol were placed in a hard-glass tube, which was then sealed. It was heated for two hours at a temperature of 160° in a Carius furnace. The reaction took place readily, a dark red liquid being formed. The pressure in the tube, calculated from the vapor tension of methyl alcohol at 160°, was at least 30 atmospheres The decomposition probably takes place at a pressure much lower than this. The product of the decomposition was converted into the amide, which was found to be the *methoxy* amide. This was the *only* amide formed.

This experiment completes the chain of evidence showing that low pressure favors the hydrogen reaction and high pressure the methoxy reaction. This is in accordance with the results obtained in previous investigations carried on in this laboratory. Having arrived at these results with methyl alcohol, the idea of investigating the action of ethyl and propyl alcohols under the same conditions naturally presented itself.

[1] This Journal **15**, 320.

Action of Ethyl Alcohol on Paradiazobenzenesulphonic Acid at Ordinary Pressure.

For this and the succeeding experiments with this alcohol, ethyl alcohol of 95 per cent., distilled from lime, was used. 10 grams of the diazo compound and 200 cc. of ethyl alcohol were placed in a balloon flask, to which was attached an inverted condenser. Upon applying heat the alcohol assumed a yellow color, which gradually passed through pink to a deep red. The odor of aldehyde was plainly perceptible during the course of the experiment. About two hours were required for complete decomposition. The deep red liquid was then freed from the alcohol, which remained unacted upon, and after purification with animal charcoal was converted into the amide. But *one* amide was found, and its crystal form and melting-point showed it to be benzenesulphonamide.

Action of Ethyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 350 *mm.*

10 grams of the diazo compound and 200 cc. ethyl alcohol were placed in the pressure-flask. Heat was applied until a pressure of 350 mm. was indicated by the manometer. The pressure was held at this point until the decomposition was complete, one and a half hours being required for this purpose. The product of decomposition was treated as before and converted into the amide. Only *one* amide was formed, and this was benzenesulphonamide.

Action of Ethyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 840 *mm.*

10 grams of the diazo compound and 200 cc. ethyl alcohol were placed in the pressure-flask. The decomposition took place at a pressure of 820–840 mm., about seventy minutes being required for complete decomposition. The product was converted into the amide as above. Only *one* amide was found. This was benzenesulphonamide.

These experiments show that when ethyl alcohol acts upon diazobenzenesulphonic acid under the varying conditions of pressure given above, the ethoxy reaction does not take place. Ador and Victor Meyer decomposed diazobenzenesulphonic acid with ethyl alcohol about twenty years ago.[1] They found only the hydrogen product.

[1] Ann. Chem. (Liebig) **159**, 8.

Action of Propyl Alcohol on Paradiazobenzenesulphonic Acid at Ordinary Pressure.

5 grams of the diazo compound and 50 cc. propyl alcohol, boiling-point 96°, were placed in a small flask connected with an inverted condenser. The flask was placed in a bath of a concentrated solution of sodium chloride. The bath was heated to boiling for two hours. The decomposition may have been complete, and probably was, before this time, but owing to the fact that the diazo compound contained some sulphanilic acid which had escaped the diazotizing action, and that the product of the decomposition was a black tarry liquid, it was difficult to tell accurately when the decomposition was complete. The excess of propyl alcohol was distilled off, the tarry residue diluted with water and filtered. The solution filtered with great difficulty, and a residue was left on the filter which was not sulphanilic acid. The filtrate was a muddy-looking liquid, holding something in suspension which could be removed only by repeated filtering. Upon adding a solution of barium hydroxide to neutralize the acid or acids formed, and to precipitate the sulphuric acid formed from the decomposition of the sulphonic acid, a tarry deposit was obtained. This was filtered off, and carbon dioxide passed into the solution to precipitate the excess of barium hydroxide. The barium carbonate was then filtered off and the solution boiled to decompose any acid barium carbonate which might have been formed. Sodium carbonate was then added, and after filtering, the solution was evaporated to dryness. The sodium salt was of a dark brown color. This was treated with phosphorus pentachloride. The residue obtained after driving off the phosphorus oxychloride was a black oily liquid weighing 2 grams. This was treated with an excess of concentrated ammonium hydroxide. After evaporating off the excess, a black gummy substance was obtained. This was dissolved in hot water and treated with animal charcoal, small quantities only being used. It did not crystallize well from water; mixed with small white crystals there was always found a dark gummy substance. This mixture was recrystallized from alcohol, the alcohol removed, and the crystals redissolved in hot water. By this means they can be obtained pure. An examination showed them to be the crystals of benzenesulphonamide. No other amide was found.

When paradiazobenzenesulphonic acid is decomposed with propyl alcohol, a much more serious breaking down occurs than when the decomposition is effected with either methyl or ethyl alcohol. The amide, or rather the acid from which the amide is derived, can be obtained only in very small quantities, while the principal product of the decomposition, so far as quantity is concerned, is the tarry matter referred to above.

Action of Propyl Alcohol on Paradiazobenzenesulphonic Acid at a Pressure of 700 mm.

The object of this experiment was to determine what effect a higher pressure than that used in the preceding experiment would have on the decomposition products. I desired to effect the decomposition at a pressure of about 840 mm. The experiment was carried out in the usual way. Upon applying heat the decomposition began almost immediately, and before the pressure could be raised to 840 mm. it was complete, the manometer indicating 700 mm. The product of this action was a black tarry liquid. It was purified with animal charcoal, then treated with barium hydroxide and converted into the amide as above. But *one* amide, benzenesulphonamide, was formed, and that in very small quantity.

The results obtained with ethyl and propyl alcohols are in accordance with those on record. Experiments with other alcohols were not made, the results obtained being considered sufficient for the purposes of this investigation.

The acid of which methoxybenzenesulphonamide is a derivative has been prepared by Kekulé,[1] and by Cahours and Annaheim ;[2] and some of its derivatives by Haitinger.[3] I desired to prepare the acid in the manner described by Kekulé from anisol (methylphenyl ether) and sulphuric acid, in order that the amide made from it might be compared with the amide obtained from the acid formed by the decomposition of diazobenzenesulphonic acid with the methyl alcohol.

Preparation of Anisol.—In view of the observations of Remsen and Orndorff[4] that phenetol is the principal product of the action of ethyl alcohol on diazobenzene nitrate, it was thought probable that anisol would be formed by the action of methyl alcohol.

[1] Ztschr. f. Chem. **1867**, 201.
[2] Monatshefte **4**, 173.
[3] Ann. Chem. (Liebig) **172**, 47.
[4] This Journal **9**, 387.

This was found to be the case, and indeed the method can be recommended for the preparation of anisol.

The diazo compound and absolute methyl alcohol were heated together in a flask connected with an inverted condenser. The decomposition began almost immediately, and after the temperature had been raised to 45° the burner was removed. The decomposition continued without further application of heat. I afterwards found that the decomposition will take place as well without the application of heat. If methyl alcohol and diazobenzene nitrate be brought together and allowed to stand, decomposition begins in 10–15 minutes, with elevation of temperature. After the action was complete the contents of the flask were subjected to distillation. Anisol and methyl alcohol passed over. The alcohol had a yellow color and an aromatic odor, due to the presence of anisol. This distillate was treated with about six times its volume of a saturated solution of sodium chloride. On standing, a light yellow oil collected at the surface. In order to obtain the last portions of anisol, the sodium-chloride solution was distilled; methyl alcohol and a small quantity of anisol passed over, but in this case the oil collected in the bottom of the receiver in globules and could easily be obtained. To the contents of the flask from which the anisol and methyl alcohol had been obtained in the first instance, sodium hydroxide was added to alkaline reaction. The flask was then heated and steam passed into it, when a small quantity of anisol passed over with the water vapor. Sulphuric acid was then added to the mixture in the flask to acid reaction and it was again subjected to distillation with steam. Orthonitrophenol was formed in the receiver and condenser. The residue in the flask was not examined further. The anisol obtained was purified by treating with fused calcium chloride and then distilled. It boiled at 151°.

Action of Sulphuric Acid on Anisol.—The anisol was poured slowly into an excess of ordinary concentrated sulphuric acid. It apparently dissolved, with a slight elevation of the temperature of the mass. It was then heated for half an hour on the water-bath. The mixture was neutralized with barium carbonate and converted into the potassium salt. This solution was evaporated to dryness. The dried substance is exceedingly hard, brittle and hygroscopic. To preserve it in the dry condition it must be kept in a desiccator. This potassium salt was converted into the sulphonic chloride by treatment with phosphorus pentachloride. At the ordinary tem-

perature no action takes place, and it is necessary to apply heat. After distilling off the phosphorus oxychloride the residue was treated with water. No oil was observed. I then added ether in order to extract any sulphonic chloride which might have been formed. Upon pouring off the ethereal solution and distilling, beautiful crystal plates, of a pleasant odor, somewhat suggestive of the sulphonic chlorides in general, were obtained. These were supposed to be the crystals of either ortho- or paraanisolsulphonic chloride. The orthochloride melts at 55° (Haitinger). The crystals that I obtained melted at 86°. The following analysis of the compound was then made:

I. .10825 gram of the substance gave .1023 gram of silver chloride, corresponding to 23.37 per cent. of chlorine.

II. .23469 gram of the substance gave .21665 gram of silver chloride, corresponding to 22.83 per cent. of chlorine (Carius' method).

I. .2184 gram of the substance gave .2244 gram of carbon dioxide, corresponding to 28.02 per cent. of carbon.

II. .2880 gram of the substance gave .0694 gram of water, corresponding to 2.67 per cent. of hydrogen.

I. .23469 gram of the substance gave .3623 gram of barium sulphate, corresponding to 21.21 per cent. of sulphur (Carius' method).

For $C_6H_4.OCH_3.SO_2Cl$:

		Theory.	Found. I.	Found. II.
C_7	83.79	40.60	28.02	...
H_7	7.00	3.39	...	2.67
O_3	47.88	...	...	...
S	31.98	15.52	21.21	...
Cl	35.37	17.17	23.37	22.83
	206.02			

Evidently the compound analyzed was not anisolmonosulphonic chloride. It was the disulphonic chloride. This result was unexpected, since Zervas,[1] in order to make the disulphonic acid, treated anisol with *fuming* sulphuric acid. I obtained it as described above by using ordinary concentrated acid and heating for a half-hour on the water-bath.

Análysis for $C_6H_3.OCH_3(SO_2Cl)_2$:

[1] Ann. Chem. (Liebig) **103**, 342.

		Theory.	Found. I.	II.
C_7	83.79	27.54	28.02	...
H_6	6.00	1.97	...	2.67
O_5	79.80	...	...	...
S_2	63.96	21.02	21.21	...
Cl_2	70.74	23.25	23.37	22.83
	304.29			

Lack of time prevented me from repeating the experiment with anisol and sulphuric acid. A portion of the disulphonic chloride obtained as described above was converted into the amide by treatment with ammonium hydroxide. Upon crystallizing the product, apparently crystals of two different kinds were found. They were not investigated.

Wichelhaus[1] states that if benzenesulphonamide be warmed with phosphorus pentachloride, benzenesulphondichlorphosphamide is formed. It was desirable to know how methoxybenzenesulphonamide would act under similar conditions. The following experiment was made to determine this action:

Two grams of methoxybenzenesulphonamide were treated with the proper proportion of phosphorus pentachloride. No action took place at the ordinary temperature. Upon applying heat, action began at once, and hydrochloric acid was given off. The oily product obtained was poured on a porous plate and allowed to stand over sulphuric acid for about two weeks (Wichelhaus). It was then dissolved in anhydrous ether and allowed to stand. Although several attempts were made to obtain crystals, they were unsuccessful. When the ether was allowed to evaporate off slowly, a clear viscous liquid was obtained, which, upon being exposed to the air, gave off hydrochloric acid. When the product of the decomposition of the amide and phosphorus pentachloride was allowed to stand in moist air, or when water was added to it, decomposition began at once and the substance was converted back to the amide. In this respect its behavior is similar to that of benzenedichlorphosphamide.

Action of Nitric Acid on Methoxybenzenesulphonamide. — 4.7 grams of methoxybenzenesulphonamide were added slowly to 15 cc. of fuming nitric acid. The action was very energetic. For this reason only a small quantity of the amide should be added at a time. Upon diluting the nitric acid solution with water

[1] Ber. d. chem. Gesell. **2**, 502.

a precipitate or emulsion of minute globules of oil was obtained. The solution was diluted still further and heated to boiling. The oil dissolved with difficulty. Upon cooling, beautiful crystals of slender needle-shape, somewhat similar to those of the amide, separated. A determination of the melting-point, which was found to be 88°, showed that the substance was not the amide. A test for sulphur failed to show its presence. This, together with the form of the crystals, led me to believe that the substance was metadinitrobenzene, and this proved to be the case.

The melting-point was 88° (uncorrected). That of metadinitrobenzene is 89.9° (corrected).[1] Its solubility in hot water, alcohol and ether agreed with that of metadinitrobenzene in these reagents.

The preceding experiment was repeated, a more dilute acid—ordinary concentrated nitric acid—being employed. The action was not quite so energetic, but otherwise the same results were obtained. With more dilute acid the reaction does not take place. The amide dissolves, but, on cooling, it crystallizes out unchanged. These experiments show that the paramethoxybenzenesulphonamide is very susceptible to the action of nitric acid. Not only are the methoxy and sulphonamide groups, which are in the para position, replaced by the nitro group, but apparently a rearrangement of the parts takes place, the nitro groups entering the *meta* position.

Summary of Results.

I. When paradiazobenzenesulphonic acid is decomposed with methyl alcohol under diminished pressure, only the hydrogen product is obtained.

II. At ordinary pressure both the hydrogen and methoxy reactions take place.

III. At a pressure of 350 mm. both reactions take place.

IV. At a pressure of 850 mm. both reactions take place, the methoxy compound predominating.

V. At a pressure of about 30 atmospheres the methoxy reaction alone takes place.

VI. When ethyl alcohol is used in the decomposition of paradiazobenzenesulphonic acid, at various pressures up to 850 mm., only the hydrogen product is obtained.

VII. When propyl alcohol is used under the same conditions the hydrogen product only is formed.

[1] Griess: Berichte **11**, 625.